

The University of Chicago

THE RAMAN EFFECT AND THE CARBON-CHLORINE BOND

A PART OF THE DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF PHYSICAL
SCIENCES IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By
ROBERT RAY HAUN

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THE RAMAN SPECTRUM OF GERMANIUM TETRACHLORIDE

By R. R. HAUN

The Raman spectrum of germanium tetrachloride was obtained by the method described in the next paper of this series. The frequencies of the Raman lines are given in Table I.

Considerable work, both experimental and theoretical, has been done upon the problem of the vibrational frequencies of molecules of the type

TABLE I

THE RAMAN LINES OF GERMANIUM TETRACHLORIDE

Raman	Raman lines, exciting lines and displacements in cm. ⁻¹				D
	Excit.	D	Raman	Excit.	
22487 (1)	22938	451	23112 (5)	22938	174
22544 (10)	22938	394	23337 (6)	22938	399
22595 (1)	22995	400	24309 (6)	24705	396
22768 (6)	22938	170	24535 (2)	24705	171
22808 (6)	22938	130	24571 (2)	24705	134
23070 (5)	22938	132			

SUMMARY OF DISPLACEMENTS IN ORDER OF INTENSITY

397 (10), 132 (6), 171 (6), 451 (or 508) (1)

XY₄, which contain five atoms. Table II gives a comparison of the wave numbers for the tetrachlorides of carbon, silicon, titanium and tin, with those of germanium.

TABLE II

RAMAN FREQUENCIES OF TETRAHALIDES

	CCl ₄ (6)	SiCl ₄ (14)	TiCl ₄ (22)	GeCl ₄ (32)	SnCl ₄ (50)	CBr ₄	SnBr ₄
ω_2 (?)	217 (8)	151 (5)	(120 (4))	132 (6)	104 (5)	123 (2)	64 (2)
ω_4 (a)	313 (8)	221 (5)	(144 (1))	171 (6)	134 (6)	183 (4)	88 (4)
ω_1 (?)	459 (8)	452 (10)	(386 (6))	397 (10)	366 (10)	265 (5)	220 (4)
ω_3 (a)	760 (3)	607 (2)	(497 (2))	451 (1)	404 (6)	667 (3b)	279 (3)
	791 (3)			(or 508)			
	1537 (1)						

The data for all of the substances with the exception of germanium tetrachloride are taken from the compilation by Kohlrausch.¹

¹ Kohlrausch, "Der Smekal-Raman-Effekt," Berlin, 1931.

In this table the chlorides are arranged in increasing order of the atomic numbers of the fourth group elements. The values for germanium tetrachloride appear to be too high in comparison with those of titanium and tin. However, this discrepancy is partly fictitious, since titanium belongs to another subdivision of group 4 of the periodic system² than germanium and tin. The normal term is 3F_2 for titanium, but 3P_0 for all of the other elements of this group.

Figure 1 exhibits the following interesting relations: the wave numbers for any one of the types of frequencies (ω_1 , ω_2 , ω_3 or ω_4) are nearly linear with respect to atomic number (1) for carbon, silicon and titanium, and (2) (except for W_3) for silicon, for germanium and tin.

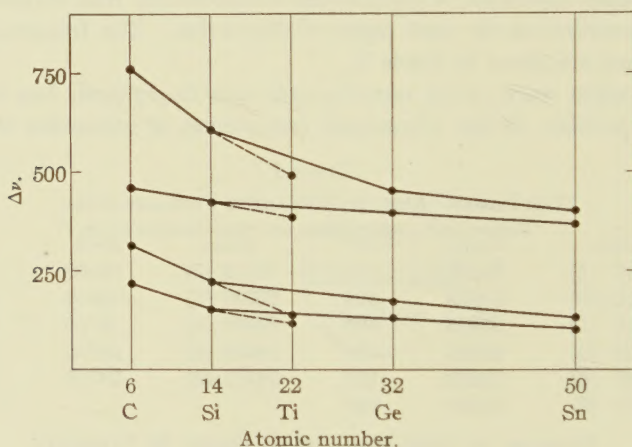


Fig. 1.—Raman frequencies for tetrachlorides (in cm^{-1}). The highest frequency for germanium may be 508 cm^{-1} instead of the value plotted. If this is true the uppermost line is also linear from Si to Sn.

The theory of the spectra of molecules of the type XY_4 has been developed for methane by Dennison³ and for tetrahalides by Schaeffer⁴ on the assumption of central forces. Trumpy⁵ has shown that the three constants of the theory can be adjusted in such a way as to give a moderately good agreement with the observed data. Urey and Bradley⁶ use a more accurate theory which considers forces which act along the "valence

² Harkins and Hall, *J. Am. Chem. Soc.*, **38**, 169 (1916).

³ Dennison, *Astrophys. J.*, **62**, 84 (1925).

⁴ Schaeffer, *Z. Physik*, **60**, 586 (1930).

⁵ Trumpy, *ibid.*, **66**, 790 (1930).

⁶ Urey and Bradley, *Phys. Rev.*, **38**, 1969 (1931).

bonds," perpendicular to them, and also repulsive forces between the halogen atoms. Both Trumpy, and Urey and Bradley, obtain the poorest agreement in the case of titanium tetrachloride.

The frequencies ω_1 and ω_2 correspond to optically inactive vibrations which do not affect the electrical moment. The vibration for ω_1 is along the valence directions of the tetrahedron, and all the halogen atoms are supposed to move outward (or inward) simultaneously in such a way as to keep the resultant force upon the central atom equal to zero. In the vibration for ω_2 the halogen atoms are supposed to move on the surface of a sphere for which the atom X is the center. The frequencies ω_3 and ω_4 correspond to vibrations in which the symmetry of the molecule is not preserved, so the electrical moment is affected and ω_3 and ω_4 are optically active.

The writers are indebted to Professor Warren C. Johnson for the germanium tetrachloride, and to a Grant-in-Aid of the National Research Council for the spectrograph used in this investigation.

Summary

1. The Raman spectrum of germanium tetrachloride is found to correspond to four displacements of wave number with values as follows

$$\omega_2 = 132 (6), \omega_4 = 171 (6), \omega_1 = 397 (10) \text{ and } \omega_3 = 451 (1)$$

(with a possibility that ω_3 is 508). The numbers in parentheses denote the relative intensities, and ω_1 and ω_2 designate, according to the theory, optically inactive and ω_3 and ω_4 , optically active frequencies.

THE VIBRATION OF ATOMS AT THE END OF ORGANIC MOLECULES: RAMAN EFFECT AND THE CARBON-CHLORINE BOND

BY R. R. HAUN

1. Introduction

This investigation is a continuation of a study¹ of the effect of the length of an organic molecule and of a splitting of the hydrocarbon chain upon the vibration of an atom attached at the end of the molecule.

In the spectra of the halides of the paraffins the Raman frequency which is on the whole by far the most intense is represented in wave numbers in cm^{-1} by the values 712, 603 and 522 for the methyl chloride, bromide, and iodide, and by 650, 566 and 500 for the corresponding normal compounds which contain more than one carbon atom.

These values may be supposed to give the frequency of (longitudinal) vibration of the halogen atom at the end of the molecule with respect to the adjacent $-\text{CH}_2-$ group. This frequency is in the methyl halides 2.13×10^{13} per second between carbon and chlorine, 1.81×10^{13} between carbon and bromine and 1.60×10^{13} between carbon and iodine. If more than one carbon atom is present these values are reduced to 1.96×10^{13} for chlorine, 1.70×10^{13} for bromine and 1.53×10^{13} for iodine. For comparison it may be stated that the frequency of vibration of the carbon atom in diamond is 3.7×10^{13} per second according to the simple theory of Lindemann.

The equation which gives the energy (ϵ^v) of the vibrational quantum number v ($= 0, 1, 2, 3, \dots$) is, for an electronic state (e)

$$\epsilon^v = hc[\bar{\omega}_e(v + 1/2) - \bar{\omega}_e x_e(v + 1/2)^2 + \dots] \quad (1)$$

It may be assumed that these Raman lines are usually produced by a net decrease (or increase in anti-Stokes lines) of unity in the vibrational quantum number, and that the transitions occur either to or from the zero state. Under these conditions it is justifiable to use merely the first term in v of the above equation since the error introduced in this way is small, probably less than one per cent. If the final Δv is two, then the error is larger, but still relatively small. In this paper $\bar{\omega}$ will be used to represent a wave number in cm^{-1} and ω , a frequency in sec^{-1} .

On the above basis it may be assumed that the mechanical frequency ω_0 is, for a value of $\Delta v = \pm 1$, related approximately by the equation

$$\Delta\nu = \omega_0(v' - v'') = \frac{1}{2\pi} \left(\frac{f}{\mu} \right)^{1/2} (v' - v'') \quad (2)$$

¹ Harkins and Bowers, *J. Am. Chem. Soc.*, **53**, 2425 (1931).

to the Raman frequency ($\Delta\nu$), which is associated with the vibration. For $\nu' - \nu'' = \pm 1$ this becomes

$$\Delta\nu = \pm \frac{1}{2\pi} \left(\frac{f}{\mu} \right)^{1/2} \quad (3)$$

the equation of the classical theory, in which μ is the mutual mass ($1/\mu = 1/m_1 + 1/m_2$) of the bodies which vibrate, and f is the force constant in the equation $P = f x$, in which P is the restoring force and x the displacement. A discussion of the probable values of the (valence) force constant will be given after the data have been presented.

2. Experimental Procedure

The apparatus is essentially the same as that used by Harkins and Bowers. The substance to be investigated was put into a bulb which is sealed to the Raman tube. The system was evacuated and sealed off, and the liquid then distilled into the Raman tube. The tube was placed vertically in a cylindrical container and a set of "condensed" mercury vapor arcs placed alongside the tube. The Raman tube and lamps were kept cooled by a stream of distilled water, which had been cooled previously by passing through a coil kept in ice. In this way it was possible to prevent distillation back into the side bulb, and consequently to use liquids of lower boiling point than in the previous work. In general, the chlorides used suffer no photochemical decomposition so that it was not necessary to use the filters which were required with the bromides and iodides.

The scattered light passed through a window in the bottom of the container and was reflected by a right angle prism into the spectrograph. The instrument used was a large Steinheil three glass prism spectrograph, which gives large dispersion and consequently affords greater accuracy in the determination of the frequencies. The dispersion obtained was 6 Å. per mm. at 4000 Å. and 25 Å. per mm. at 5500 Å., which was the range over which the experiments were conducted. Since the range was small, not as many Raman lines were obtained as by some other experimenters, but it was not thought necessary to repeat the experiments with another setting of the instrument, since the important values were obtainable with one setting. The large dispersion also accounts for the absence of some of the weaker lines, since the intensity is decreased.

The approximate wave length of each line was first obtained by direct comparison with the spectrum of the iron arc. The more exact values were obtained by measuring with the comparator and the use of the Hartmann formula. These were converted to frequencies and the differences between these and all the possible mercury exciting frequencies were calculated. The assignment to exciting frequencies was based upon the recurrence of the same difference and also to some extent upon the relative intensities.

TABLE I
RAMAN LINES, EXCITING LINES AND DISPLACEMENTS IN CM.⁻¹

Raman	Exct.	Δ	Raman	Exct.	Δ	Raman	Exct.	Δ
Ethyl Chloride								
19969 (2)	22938	2969	21830 (2)	24705	2875	22280 (10)	22938	658
20008 (2)	22938	2930	21873 (2)	22938	1065	22601 (3)	22938	337
21740 (4)	24705	2966	21974 (1)	22938	964	24047 (6)	24705	658
21772 (4)	24705	2933						
<i>n</i> -Propyl Chloride								
19982 (4)	22938	2956	22212 (8)	22938	727	24395 (1)	27353	2958
21486 (5)	22938	1452	22290 (10)	22938	648	24419 (1)	27353	2934
21749 (6)	24705	2957	22573 (8)	22938	366	24431 (1)	27388	2957
21773 (6)	24705	2933	23927 (1)	24705	779	24458 (4)	27388	2931
21834 (5)	24705	2872	23981 (2)	24705	725	24478 (3)	27353	2875
22151 (7)	22938	787	24058 (4)	24705	643			
<i>n</i> -Butyl Chloride								
21738 (2)	24705	2967	22282 (10)	22938	656	24425 (8b)	27388	2964
21764 (2)	24705	2942	22613 (1)	22938	325	24451 (8b)	27388	2937
21802 (4)	24705	2903	22645 (1)	22938	293	24486 (8b)	27388	2903
21832 (6)	24705	2875	24050 (2)	24705	655	24356 (1)	27388	3032
22219 (2)	22938	719	24389 (5b)	27353	2964			
<i>n</i> -Amyl Chloride								
19972 (2)	22938	2967	21738 (4)	24705	2967	22207 (8)	22938	731
19996 (2)	22938	2943	21764 (4)	24705	2941	22280 (10)	22938	658
20024 (2)	22938	2914	21797 (2)	24705	2908	22428 (1)	22938	456
20060 (4)	22938	2877	21835 (8b)	24705	2870	22588 (1)	23039	451
21489 (10b)	22938	1450	21968 (1)	22938	970	23253 (4)	24705	1452
21553 (3)	24516	2963	22046 (1)	22938	893	23977 (1)	24705	729
21631 (3)	24516	2885	22146 (1)	23039	893	24048 (8)	23705	657
						24145 (1)	25592	1447
Isopropyl Chloride								
20009 (1)	22938	2929	21835 (3)	24705	2870	22598 (6)	22938	340
21491 (1)	22938	1447	21876 (3)	22938	1062	23256 (1)	24705	1450
21679 (1)	22938	1259	21975 (1)	22938	963	23646 (1)	24705	1060
21716 (2)	24705	3026	22052 (5)	22938	886	23187 (1)	24705	888
21767 (5)	24705	2938	22320 (10)	22938	618	24088 (7)	24705	617
21787 (5)	24705	2918	22512 (6)	22938	427			
Isobutyl Chloride								
19958 (1)	22938	2980	21829 (3)	24705	2876	23973 (3)	24705	733
20058 (1)	22938	2880	21977 (1)	22938	962	24014 (2)	24705	691
21362 (1)	24335	2973	22117 (3)	22938	821	24140 (3)	24705	565
21483 (1)	22938	1455	22205 (10)	22938	733	24408 (1)	27388	2980
21602 (1)	22938	1336	22246 (9)	22938	692	24433 (1)	27388	2955
21723 (2)	24705	2982	22371 (2)	22938	567	24476 (1)	27388	2912
21754 (2)	24705	2951	22504 (2)	22938	434			
21791 (2)	24705	2915	22599 (1)	22938	339			

TABLE I (*Concluded*)

Raman	Exct.	Δ	Raman	Exct.	Δ	Raman	Exct.	Δ				
Isoamyl Chloride												
19972	(3)	22938	2966	21978	(2)	22938	960	23879	(1)	24705	826	
21484	(2)	22938	1454	22107	(4)	22938	832	23950	(1)	24705	755	
21550	(1)	24516	2965	22183	(2)	22938	755	24049	(2)	24705	656	
21596	(1)	24516	2920	22214	(2)	23039	826	24238	(1)	24705	412	
21643	(1)	24516	2874	22279	(4)	22938	659	24356	(1)	27388	3032	
21735	(8)	24705	2970	22380	(1)	23039	660	24388	(6)	27353	2965	
21771	(4)	24705	2934	22521	(1)	22938	418	22423	(10b)	27388	2966	
21834	(7)	24705	2871	22662	(1)	25592	2930	24458	(5)	27388	2930	
									24483	(5)	27388	2870
Sec.-butyl Chloride												
20010	(4)	22938	2928	22269	(2)	22938	670	23329	(2)	24705	1377	
21489	(1)	22938	1449	22306	(1)	22938	632	24039	(1)	24705	667	
21586	(1)	24516	2930	22333	(4)	22938	605	24100	(1)	24705	606	
21724	(4)	24705	2981	22417	(1)	22938	522	24148	(1)	25592	1444	
21776	(8)	24705	2930	22475	(2)	22938	463	24364	(3)	27388	3025	
21829	(3)	24705	2876	22558	(2)	25592	3034	24420	(10b)	27388	2968	
22094	(1)	22938	844	22609	(2)	25592	2983	24460	(10b)	27388	2929	
Tert.-butyl Chloride												
19295	(1)	20155	859	21581	(2)	23039	1458	22694	(2)	24705	1911	
19471	(1)	20336	866	21725	(7)	24705	2980	24131	(1)	22592	1461	
19952	(2)	22938	2986	21775	(8)	24705	2930	24143	(9)	24705	563	
20007	(2)	22938	2932	22066	(1)	24516	2450	24363	(2)	27388	3026	
20452	(4)	22938	2487	22126	(5)	22938	812	24405	(5)	27388	2983	
20490	(1)	22938	2449	22369	(10)	22938	569	24421	(5)	27388	2967	
20839	(2)	22938	2099	22565	(2)	25592	3026	24459	(9)	27388	2930	
21479	(1)	22938	1460	22626	(2)	25592	2966					
Tert.-amyl Chloride												
19954	(1)	22938	2984	22139	(1)	22938	799	22636	(1)	25592	2990	
20000	(1)	22938	2938	22162	(1)	25093	2932	23256	(3)	24705	1449	
21483	(4)	22938	1455	22320	(3)	22938	619	24142	(8)	24705	563	
21728	(7)	24705	2977	22377	(8)	22938	562	24409	(10)	27388	2980	
21773	(8)	24705	2933	22567	(3)	25592	3025	24451	(10)	27388	2938	
21816	(2)	22938	1123	22602	(1)	22938	336					
Allyl Chloride												
19979	(2)	22938	2959	21716	(1)	23039	1323	23291	(3)	24705	1414	
19910	(1)	22938	3029	21740	(7)	24705	2965	23411	(2)	24705	1295	
21293	(9)	22938	1645	22201	(10)	22938	737	23447	(2)	24705	1258	
21522	(5)	22938	1416	22346	(8)	22938	592	23501	(2)	24705	1204	
21607	(1)	22938	1330	22523	(5)	22938	416	23771	(1)	24705	934	
21639	(4)	22938	1299	22644	(4)	22938	295	23966	(7)	24705	739	
21678	(8)	22938	1260	22695	(1)	24335	1640	24112	(3)	24705	593	

3. Experimental Data

Table I shows the compounds used, the values of the Raman frequencies obtained, the exciting frequencies to which they have been assigned, and

the frequency displacements. The intensities given are rough estimates made by arbitrarily assigning an intensity of 10 to the strongest Raman line on each plate, and estimating a comparative value of the others on that plate in terms of it.

A summary of the various displacements for the above compounds is given in Table II. Following this, in Table III, are given the values attained by other workers for those compounds of the above series which

TABLE II

RAMAN DISPLACEMENTS IN CM.^{-1} FOR A SERIES OF ORGANIC CHLORIDES (HARKINS AND HAUN)

Ethyl	<i>n</i> -Propyl	<i>n</i> -Butyl	<i>n</i> -Amyl	Isopropyl	Isobutyl
337 (3)	366 (8)	294 (1)	454 (1)	340 (6)	339 (1)
		325 (1)		427 (6)	434 (2)
658 (10)	648 (10)	655 (10)	658 (10)	618 (10)	566 (3)
					691 (9)
	726 (6)	(719) (2)	730 (8)		733 (10)
	783 (7)				821 (3)
			893 (1)	887 (5)	
964 (1)			970 (1)	(963) (1)	962 (1)
1065 (2)				1063 (3)	
				1259 (1)	1336 (1)
	1452 (5)		1450 (10)	1448 (1)	1455 (1)
2875 (2)	2872 (7)	2874 (5)	2877 (8)	2870 (3)	2878 (3)
		2903 (8)	2911 (2)	2918 (5)	2914 (2)
2931 (4)	2930 (6)	2939 (8)	2941 (4)	2934 (3)	
2967 (4)	2956 (6)	2964 (8)	2967 (4)		2953 (2)
		3032 (1)		3026 (2)	2980 (1)
Isoamyl	<i>Sec.</i> -butyl	<i>Tert.</i> -butyl	<i>Tert.</i> -amyl	Allyl	
	463 (2)			295 (4)	
415 (1)	(522) (1)		(336) (1)	416 (5)	
657 (4)	605 (4)	566 (10)	562 (8)	593 (8)	
	668 (2)		(619) (3)		
755 (2)	(632) (1)		(799) (1)	738 (10)	
828 (4)	(844) (1)	(812) (5)			
		862 (1)			
(960) (2)				934 (1)	
			(1123) (2)	1204 (2)	
				1259 (8)	
				1297 (4)	
	(1377) (2)			1327 (1)	
1454 (2)	1446 (1)	1460 (1)	1452 (4)	1415 (5)	
		(1911) (2)			
2872 (7)	(2876) (3)	(2099) (2)		1645 (9)	
(2920) (1)		2449 (1)			
2931 (5)	2929 (10)	2930 (9)	2935 (10)		
2965 (10)	(2968) (10)	2966 (2)	2978 (10)	2962 (7)	
	2982 (4)	2983 (7)	2987 (2)		
3026 (1)	3029 (3)	3026 (2)	3025 (3)	3028 (1)	

TABLE III

RAMAN DISPLACEMENTS IN CM.^{-1} FOR ORGANIC CHLORIDES (FROM KOHLRAUSCH'S "DER SMEKAL-RAMAN EFFEKT")

Methyl	Ethyl	<i>n</i> -Propyl	<i>n</i> -Butyl	Isopropyl	Isobutyl	<i>Terl.</i> -butyl	Allyl
			302 (3)		157 (0)		
	337 (5)	365 (4)	333 (4)	340 (3)	238 (0)	299 (3)	301 (3)
	438 ($1\frac{1}{2}$)	(418) (2)		426 (2)	340 (1)	368 (3)	
			469 (2)	490 (0)	433 (1)		408 (3)
712 (10)	655 (10)	651 (5)	650 (8)	614 (5)	528 (0)		514 (1)
		725 (4)	722 (4)		696 (3)	546 (6)	589 (4)
			809 (4)		738 (4)		735 (2)
		850 (2)	871 (3)		815 (1)	806 (3)	
		892 (2)	898 (1)	886 (2)	867 (0)		
	966 (4)		928 ($1\frac{1}{2}$)		956 (2)		932 (2)
						1017 (1)	1032 (1)
1098 (2)	1071 (3)	1028 (3)	1055 (3)	1060 (2)			
		(1105) (0)	1107 (6)	1158 (1)	1107 (0)		1110 (1)
							1204 (3)
	(1276) ($1\frac{1}{2}$)	(1289) (0)	1294 (4b)	1257 (2)	1230 (0)		1259 (3)
							1291 (2)
		(1339) (1)		1326 (1)	1322 (0)		1412 (3)
	1448 (4)	1446 (4b)	1464 (2)	1446 (4b)	1464 (2)	1445 (3sb)	1442 (1)
							1478 (3)
2815 (2)				(2828) (2?)			1641 (6)
	2875 (4b)	2873 (5)	2872 (3)	2864 (2)	2874 (5)	2893 (2b)	2882 (2?)
			2906 (5)	2917 (5)	2918 (0)		
	2930 (8b)	2935 (7)	2936 (4)	2932 (2)		2925 (6b)	
2955 (10)	2966 (8)	2957 (7)	2960 (5)	2964 (4)	2977 (5)		2954 (5b)
		2975 (0)					
		2998 (0)	3001 (0)				3021 (4b)
3024 (2b)		3019 (0)		3024 (0)			3087 (2b)

they have studied. These values have been taken from Kohlrausch's "Der Smekal-Raman Effekt," which contains a summary of all the results obtained by various workers up to June, 1931.

4. The Carbon-Chlorine Bond and the Vibration of Atoms at the End of an Organic Molecule. (a) Normal Compounds.—Contrary to the earlier opinion, the vibration of a bromine atom at the end of a paraffin chain has been shown to be an inner, rather than an outer, vibration.¹ That is, the vibration is largely that of the bromine atom and of the adjacent $-\text{CH}_2-$ group. This was indicated by the fact that the fundamental wave number remains practically constant at 564 cm.^{-1} as the length of the molecule is varied by a change from two to five in the number of carbon atoms. The same general constancy in frequency is found (Table IV) for the chlorine derivatives.

This table exhibits a considerable decrease of the vibration frequency at the carbon halogen bond, 54, 37 and 25 wave numbers for the chloride, bromide and iodide, respectively, as the number of carbon atoms is increased from one to two, but an approximate constancy with a further increase.

Propyl chloride appears to be somewhat anomalous in that its wave number is 10 units lower than that for ethyl chloride and 7 units lower

TABLE IV

TWO HIGHER FREQUENCIES ASSOCIATED WITH THE PRESENCE OF A HALOGEN ATOM

(1) Designates the fundamental frequency
(The numbers in parentheses represent the intensities)

	NORMAL						
	Cl (1)	Cl (2)	Δ	Br (1)	5r (2)	Δ	I (1) I (2) Δ
Methyl CH_3X	712			603 (8)			522
Ethyl $\text{CH}_3\text{CH}_2\text{X}$	658			566 (6)			497
<i>n</i> -Propyl $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$	648 (10)	726 (6)	78	563 (6) *	648 (4)	85	503 590 87
<i>n</i> -Butyl $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$	655 (10)	719 (2)	64	563 (5)	642 (2)	79	505 592 87
<i>n</i> -Amyl $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$	658 (10)	730 (8)	72	564	642	78	
ISO							
Isopropyl $(\text{CH}_3)_2\text{CHX}$	618 (10)			540			
Isobutyl $(\text{CH}_3)_2\text{CHCH}_2\text{X}$	691 (9)	733 (10)	42	572	612	60	
Isoamyl $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{X}$	657 (4)	755 (2)	98	564	619	55	
SECONDARY							
<i>Sec.</i> -butyl $\begin{matrix} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{matrix} \text{CHX}$	605 (4)	668 (2)	63	533	612	79	
TERTIARY							
<i>Tert.</i> -butyl $(\text{CH}_3)_3\text{CX}$	566 (10)			538	615	77	
<i>Tert.</i> -amyl $(\text{CH}_3)_3\text{CCH}_2\text{X}$	562 (8)	619 (3)	57	No data			
UNSATURATED							
Allyl $\text{CH}_2=\text{CHCH}_2\text{Cl}$	593 (8)	738 (10)	145	535	695	160	

than that for butyl chloride. This effect is confirmed by the data of Dadiou and Kohlrausch,² and to some extent by those of West and Farnsworth,³ who did not, however, investigate butyl chloride. The lower frequency associated here with the presence of three carbon atoms is not found for the bromide or for the iodide.

(b) **Effect of a Branching of the Chains.**—The branching of a hydrocarbon chain has a marked effect upon the frequency of vibration at the carbon-halogen bond. The relations which are exhibited are of considerable interest, and are outlined as follows where the comparisons are with respect to the frequency of the normal compounds. 1. A branching at the (α) carbon atom adjacent to the halogen atom causes a decrease of about 40 in the wave number of a chloride, and about 25 with a bromide. 2. A branching at the second (β) carbon atom causes (a) a considerable increase of frequency (about 40 wave numbers for the chloride and 16 for the bromide) if the chain divides into two (iso or secondary) at the second (β) carbon atom; (b) a large decrease of frequency, at least for tertiary amyl chloride ($\Delta\bar{\omega} \approx -100$) if the chain divides into three parts (tertiary) at the second (or β) carbon atom. 3. A branching of the chain into two methyl groups at the third (γ) carbon atom is associated with the same frequency as is found for the normal halide. 4. A double bond between the second and third carbon atoms in the allyl compounds is associated with a lowering of frequency of

² Dadiou and Kohlrausch, *Wien. Ber.*, **138**, 635 (1929).

³ West and Farnsworth, *Trans. Faraday Soc.*, **27**, 145 (1931).

about 55 for the chloride and 30 for the bromide. That these frequencies are related to the presence of the halogen atom in the molecule is shown by the fact that they are not found in the corresponding paraffins.

5. A Higher Frequency (Wave Number about 730 cm.^{-1}) Associated with the Presence of a Chlorine Atom in the Molecule.—It is found that in addition to the fundamental wave number of about 657 cm.^{-1} associated with the vibration of the halogen atom with respect to the adjacent $\text{—CH}_2\text{—}$ group, there is a higher frequency, commonly about 80 wave numbers higher, which is related in an interesting and peculiar way to the presence of the halogen atom in the molecule. The wave number involved is about 730 cm.^{-1} for either normal or iso derivatives of the paraffins (Table IV), but this frequency does not appear in the methyl or in the ethyl halide, and it is absent also for the isopropyl halide. It appears in the normal propyl and in the isobutyl halides, and in the secondary butyl derivatives. However, in the secondary compound the frequency is much lower (668 cm.^{-1}), but the fundamental frequency is also much lower (605 cm.^{-1}). The values given above are for the chlorides, but the bromides and iodides exhibit corresponding values. In the normal and iso halides the peculiar higher frequency does not appear until there are three carbon atoms in the chain, aside from those in a branch.

These relations give considerable interest to the presence or absence of the corresponding frequency in the case of the tertiary amyl halides. Here, unfortunately, the data do not entirely agree, since the frequency in question has not been found for the chlorine, but seems to have been found for the bromine derivative.

6. Lower Frequencies Possibly Associated with the Carbon-Chlorine Bond.—In general one or two additional frequencies, lower than the fundamental frequency, associated with the carbon-chlorine bond, are obtained with the compounds studied above. This is in agreement with the results obtained for the bromides by Harkins and Bowers, who sug-

TABLE V
LOWER WAVE NUMBERS CHARACTERISTIC OF THE CARBON-HALOGEN BOND (PROBABLY DUE TO A TRANSVERSE VIBRATION)

	Cl	Br	I
Ethyl	337 (4)	290	261 (8)
<i>n</i> -Propyl	366 (8)	312	285 (4)
<i>n</i> -Butyl	{ 294 (1)	280	209 (2)
	{ 325 (1)		
<i>n</i> -Amyl	...	219	250 (3)
		436	
Isopropyl	340 (6)	297	
Isobutyl	339 (2)	303	
Isoamyl		288	
<i>Tert</i> -butyl	{ 299 (3)		
	{ 368 (3)	D. K.	

gested that these lower frequencies are due to a transverse vibration at the bond, while the fundamental frequency is due to a longitudinal vibration. A larger variation is seen in the values for the chlorides than for the bromides.

West and Farnsworth also consider frequencies of this order to be due to a transverse vibration.

These values are of the general order of half those for the more characteristic vibration, but the correspondence is not at all exact.

7. Frequencies Associated with the Carbon-Hydrogen Bond and the Double Bond.—The wave numbers for the organic halides which correspond to a vibration along the carbon-hydrogen bond exhibit in general four different values of about 2870, 2930, 2965 and 3030 cm^{-1} . The first three of these are found in many other classes of derivatives, but the last is more prominent in chlorides and bromides than in most other classes of compounds. The remarkably small variation in these values in the derivatives of the paraffins will be exhibited in a later paper.

The frequency associated with the double bond in the allyl halides is 1645 cm^{-1} in the chlorides, and 1638 in the bromides.

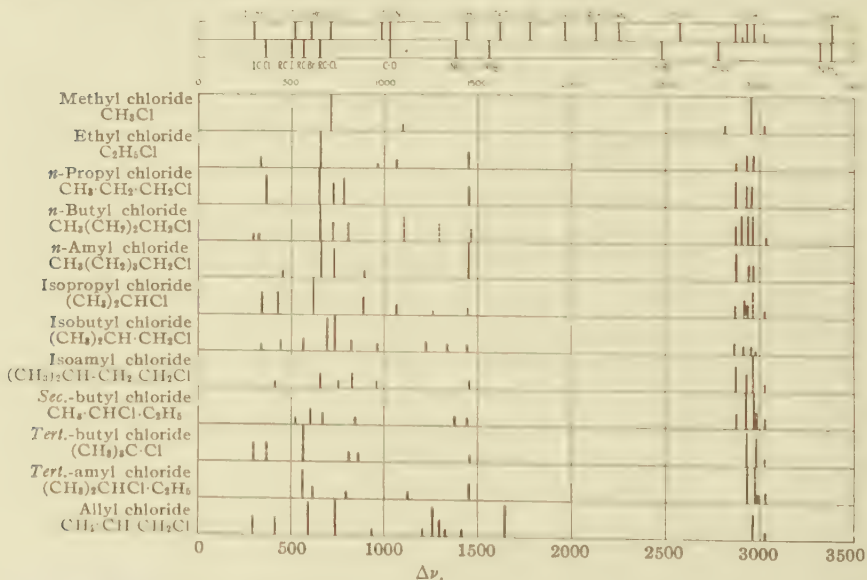


Fig. 1.—Raman frequencies for chlorides of the paraffins in cm^{-1} .

8. The Raman Frequencies of Chlorides of the Paraffins.—The relations, which have already been discussed, are summarized in Fig. 1. At the top of this figure the most characteristic Raman frequencies for various derivatives of the paraffins are summarized. The first two frequencies on the left are assumed to be due to a transverse vibration at the

carbon-chlorine bond, and the next six to longitudinal vibrations for halides (RC-X) which contain more than one carbon atom, and also for those (C-X) which contain only one carbon atom.

9. The Strength of the Carbon-Halogen Bond.—It is customary to express the strength of a chemical bond for small displacements in terms of the force constant (f) in the equation.

The values of f as calculated in an earlier paper¹ for methyl halides are given in Table VI in order to establish a basis for discussion. These values relate to a vibration in the direction of the valence bond.

The force constant (a) is calculated in the ordinary way, and it is considered that the methyl group vibrates as a unit with respect to the halogen atom. In (b) a slight, somewhat arbitrary, allowance has been made for the fact that this is not strictly true.

TABLE VI
VALUES FOR THE CARBON-HALOGEN BOND

Com- pound	Wave no., cm. ⁻¹	Frequency per second × 10 ⁻¹³	Force const. f × 10 ⁻¹¹ a	dynes/cm. b	Amplitude × 10 ³ cm.	$1/2 fa \times 10^3$	
CH ₃ Cl	712	2.135	3.136	3.02	6.7	11.6	2.0 3.5
CH ₃ Br	603	1.808	2.695	2.60	6.65	11.5	1.7 3.0
CH ₃ I	534	1.601	2.246	2.17	6.9	11.9	1.5 2.6

The force constant decreases from the chloride to the iodide. The values are much smaller than those of the single bonds listed by Dadiou and Kohlrausch which are, in 10⁵ dynes per cm., equal to 4.31 for C-C in ethane, 4.96 for C-C in methyl alcohol, and 4.89 for C-N in methylamine.

Thus if f represents the strength of the bond, the carbon-halogen bond seems to be much weaker than the most common of the other single bonds found in organic compounds. That the strength of the bond decreases rapidly from chloride to bromide to iodide, is in agreement not only with the heats of dissociation but also with the other known relations.

The meaning of the amplitude a' is definite in the classical quantum theory, but loses this definiteness in the newer quantum mechanics.

Since

$$\epsilon = fa^2/2 = (v + 1/2)\omega_0 h$$

$$a = \left(\frac{2\epsilon}{f}\right)^{1/2} = \left(\frac{(2v + 1) h\omega_0}{f}\right)^{1/2}$$

in which (ϵ) is the energy and ω_0 is the mechanical frequency. The values for this amplitude for $v = 1/2$ and $v = 3/2$ are given in Table IV.

Dadiou and Kohlrausch give the mean value of the force as $1/2 fa$, and consider this to be more characteristic of the bond than the force constant.

Unfortunately equation (3) contains two variables, the force constant and the mutual mass (μ). Thus unless the masses of the vibrating bodies are known, the equation cannot be solved.

However, the equation and the data seem to indicate that the following conclusions are approximately true. (1) In general as the length of the normal hydrocarbon chain increases from two to five carbon atoms the strength of the carbon-halogen bond remains constant. (2) The Raman frequencies alone do not show whether or not the force constant for the carbon-halogen bond decreases from the methyl to the ethyl derivative, since the lower frequency for the latter may be caused by the increase of the mutual mass due to a damping of the vibration of the adjacent $-\text{CH}_2-$ group by the remainder of the hydrocarbon chain. (3) A branching of the hydrocarbon chain seems to (a) in general lower the strength of the carbon-halogen bond, (b) increase the strength of the bond if two methyl groups are attached to the second (or β) carbon atom, (c) leave the strength of the bond the same as for the normal compound if the branching occurs at the third (or γ) carbon atom, or also presumably if it is more distant than this from the halogen atom.

The Raman wave number for butyl chloride is 655 cm.^{-1} for the normal and 566 for the tertiary butyl chloride. If this lowering of frequency for the tertiary compound is due entirely to a decrease in the strength of the bond, and not to an increase of mutual mass due to the loading up of the α -carbon atom with three methyl groups, then the force constant is lower by about 25% in the tertiary compound.

There are chemical indications which confirm the idea that the bond is considerably weaker in the tertiary than in the normal halide. For example tertiary butyl halides are almost completely hydrolyzed by shaking with water at room temperature for about ten minutes, while the normal compound is hydrolyzed only slowly by hot water.

In general the ease of hydrolysis increases and the wave number of the Raman frequency decreases in the order: normal, iso, secondary, and tertiary compound. It seems that this is the order of decreasing strength of the halogen bond.

The exceptional case of the isobutyl halides, in which the increased frequency indicates an increased strength of bond, has been mentioned earlier. The Raman effect indicates that the strength of the carbon-halogen bond increases in the order isopropyl, normal, isobutyl halide. This is the order found by Kharasch and Flenner⁴ in their study of the unsymmetrical mercuri-organic compounds.

The writers are indebted to a Grant-in-Aid of the National Research Council for the spectrograph used in this investigation.

Summary

1. It is found that the vibration at the carbon-chlorine bond in compounds of the type R-Cl , in which R is a paraffin radical, is an inner

⁴ Kharasch and Flenner, *J. Am. Chem. Soc.*, **54**, 674 (1932).

rather than an outer vibration. That is, the vibration is largely between the chlorine atom and the adjacent carbon atom with its attached hydrogen atoms. This agrees with the conclusion of Harkins and Bowers concerning the vibration at the carbon-bromine bond.

2. The fundamental carbon-chlorine frequency, which probably corresponds to a longitudinal vibration in the direction of the straight line between the carbon and the chlorine nuclei is about 710 cm.^{-1} for the methyl chloride and about 655 cm.^{-1} for normal paraffin chlorides which contain two or more carbon atoms. This latter frequency is in general lowered considerably from 605 to 560 by a not too distant branching of the paraffin chain. In isobutyl chloride the frequency is higher (690), and in the isoamyl chloride it is the same as in the normal compound.

3. The strength of the carbon-halogen bond seems to be nearly constant as the number of carbon atoms in the molecule is increased from 2 to 5. It is possible that the bond is stronger in the methyl halides, but this is uncertain, since the large difference between methyl and other normal paraffin halides may lie wholly in a smaller mutual mass in the methyl halide.

4. The bond seems to be weaker in halides of the secondary, and still weaker in those of the tertiary derivatives. It is also weak in the isopropyl halides.

5. While according to (3) a branching of the hydrocarbon chain seems in general to weaken the carbon-halogen bond, the bond seems to be strengthened by the branching in isobutyl halides, and on the whole is left unaffected if the branching occurs sufficiently distant from the halogen atom, as in isoamyl halides, in which the branching occurs at the third (γ) carbon atom.

6. A frequency about 80 wave numbers higher than the most characteristic frequency of the halides is found to exhibit a very peculiar scheme of occurrence. For example it does not appear in normal paraffins which contain less than three, and with branched chains it does not appear if the number of carbon atoms is less than four. Whether this frequency is entirely absent or merely has a very low intensity has not been determined, but its intensity in the lowest compound in which it is found is in general high, for example 10 in isobutyl chloride, while the isopropyl compound exhibits no such frequency.

7. In general a frequency about half that of the fundamental frequency, seems to be associated with the carbon-halogen bond, probably with a transverse vibration.

